Mott gap excitations in twin-free $YBa_2Cu_3O_{7-\delta}$ (T_c = 93 K) studied by RIXS

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Mott gap excitations in the high-T_c superconductor of the optimal doped $YBa_2Cu_3O_{7-\delta}$ (T_c = 93 K) have been studied by the resonant inelastic x-ray scattering method. Anisotropic spectra in the *ab*-plane are observed in a twin-free crystal. The excitation from the one-dimensional CuO chain is enhanced at 2 eV near the zone boundary of the $\boldsymbol{b}^*$ direction, while the excitation from the CuO_2 plane is broad at 1.5-4 eV and almost independent of the momentum transfer. Theoretical calculation based on the one-dimensional and two-dimensional Hubbard model reproduces the observed spectra by taking the different parameters of the on-site Coulomb energy. The fact of the Mott gap of the CuO chain site is much smaller than that of CuO_2 plane site is observed for the first time.

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Among various superconducting copper oxides $YBa_2Cu_3O_{7-\delta}$ (YBCO) is still recognized to be an important class of materials in order to elucidate the mechanism of the unconventional superconductivity with high transition temperature. However, the unique crystal structure including the one-dimensional (1D) CuO chain running along the crystalline $\boldsymbol{b}$ axis next to the double CuO_2 planes gives rise to a complexity. The CuO chain contributes to the bulk electronic properties such as the optical conductivity [1] and the dc electric conductivity [2]. Furthermore a substantial anisotropic character in the superconducting state observed in the far infrared spectra [3] and the thermal conductivity [4] suggests that the superfluid density is induced in the CuO chain, though it is generally agreed that the two-dimensional (2D) CuO_2 planes are the most important element for the superconductivity. An issue remains how the CuO chain plays a role in the superconductivity of YBCO. In other words, the instability of the 1D metals of CuO chain itself might appear as a charge modulation of the twice of the Fermi wave vector ($2k_F$) [5, 6, 7], but there might be more than the simple proximity effect of the superconductivity in the CuO_2 planes. These experimental evidences have been discussed either by the proximity effect induced chain superconductivity of the CuO_2 plane with the magnetic impurities [8] or the Friedel oscillation in the fragmentary CuO chain due to the partial oxygen depletion [9]. Therefore any experimental evidences to clarify the role of the CuO chain would make a significant contribution to understand the general consequence of high transition temperature in YBCO.

As a first step to solve this issue, the intrinsic electronic structure of the chain should be clarified. One reason why the electronic structure remains unclear is the lack of experimental tool to differentiate the electronic states of the chain from that of the plane. Here we applied the resonant inelastic x-ray scattering (RIXS) method by which the momentum dependence of the electronic excitation can be measured in contrast to the conventional optical method. The angle-resolved photoemission spectroscopy (ARPES), which also gives momentum-resolved spectra, presented the dispersion relation below E_F in the CuO chain [10], but the excitations across E_F have not been searched yet. The ARPES essentially yields the one particle spectra for the occupied states below the Fermi energy (E_F), while the RIXS gives the two particle excitations. The RIXS results of the Mott insulators, such as cuprates [11, 12, 13, 14, 15] and a manganite [16], show a peak structure in the excitation spectra crossing so called Mott gap. Furthermore, recent RIXS measurements of hole-doped manganites showed that a salient peak feature of the Mott gap remains even in the metallic state and the energy gap is partly filled at the same time [17], which really demonstrates the capability of RIXS to explore the electronic excitations in the metallic state of the transition metal oxides.

In this letter, we present the RIXS spectra of the twin-free YBCO of the optimal doping (T_c = 93 K), from which we can successfully distinguish the electronic excitations between the CuO_2 planes and the CuO chain. We also show the anisotropic x-ray absorption spectra near the Cu K-edge. It is noted that we selected the optimally doped YBCO because the anisotropy in both the normal conductivity and the superconductivity are saturated.

The experiments were carried out at the beam line 11XU of SPring-8 [18]. A Si (111) double-crystal monochromator and a Si (400) channel-cut secondary monochromator were utilized. Horizontally scattered x-rays were analyzed in energy by a spherically bent Ge

(733) crystal. Overall energy resolution is about 400 meV estimated from the full width half maximum (FWHM) of the quasielastic scattering. The $\boldsymbol{c}$-axis of the crystal was kept perpendicular to the scattering plane. Our experimental condition of the π-polarization of the incident x-ray enables us to reduce the intensity of the elastic scattering when the scattering angle (2θ) is close to 90 degree. It is crucially important to measure the low energy excitation without being disturbed by the tail of the elastic scattering, so that the Brillouin zone measured is chosen to be 2θ close to 90 degree. We used two single crystals. One is twinned crystal which is used for the incident energy (E_i) dependence, while x-ray absorption spectra and the momentum dependence of RIXS were measured for a twin-free crystal. The twin-free single crystal was grown by a crystal pulling technique [19] and detwinned under uniaxial pressure. All the spectra were collected at room temperature.

First we measured the spectra varying the energy of incident x-ray to determine a resonant energy, as shown in Fig. 1 (a). The scattering vector is fixed at $\boldsymbol{Q} = (4.5, 0, 0)$ corresponding to $\boldsymbol{q} = (\pi, 0)$ or $(0, \pi)$, where $\boldsymbol{q}$ represents the reduced wave vector in the ab-plane. A peak at 2 eV was observed at $E_i = 8990$ eV. There are another resonant features between 4 and 9 eV at higher E_i; We can see two peaks at 5.5 eV and 8 eV in the spectra of $E_i = 8996$ eV. Hereafter we fixed E_i at 8990 eV to focus on the excitation at low energy (~ 2 eV).

In Fig. 1(b), we show the x-ray absorption spectra of the twin-free crystal near the Cu-K absorption edge. The spectra were measured by the fluorescence method. Clear difference between $\boldsymbol{\epsilon} \parallel \boldsymbol{a}$ and $\boldsymbol{\epsilon} \parallel \boldsymbol{b}$ was observed. $\boldsymbol{\epsilon}$ is the polarization vector of the x-ray. From the analogy of the spectra of $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ [20], we can assign the peaks as follows. The peak at 8980 eV (labeled A in Fig. 1(b)) originates from the electric quadrupole transition from $1s$ to $3d$ states. A pair of peaks at 8984 and 8990 eV (B and C) is assigned as the dipole transition from $1s$ to $4p_\pi$ along which there is no ligand oxygen. The final state of the peak B is well-screened and that of peak C is poorly-screened. The peaks at 8997 and 9003 eV (D and E) correspond to the transition to $4p_\sigma$ whose orbital extended toward the ligand oxygens. In the case of $\boldsymbol{\epsilon} \parallel \boldsymbol{b}$, the Cu atoms in both the CuO_2 plane and the CuO chain have ligand oxygen along the direction of $\boldsymbol{\epsilon}$, and only the transition to $4p_\sigma$ is observed. On the other hand, because the Cu atoms *in the chain* have no oxygen along the $\boldsymbol{a}$-axis, the transition to the $4p_\pi$ state appears in $\boldsymbol{\epsilon} \parallel \boldsymbol{a}$. The fact that the peak at 2 eV appears resonantly at the intermediate state of $4p_\pi$ indicates that the peak originates from the chain. This inference is confirmed from the momentum dependence later.

Figures 2 show the momentum dependence of the RIXS spectra, in which $\boldsymbol{q}$ is parallel to [100], [010], and [110]. The absolute momentum transfer ($\boldsymbol{Q}$) is represented as

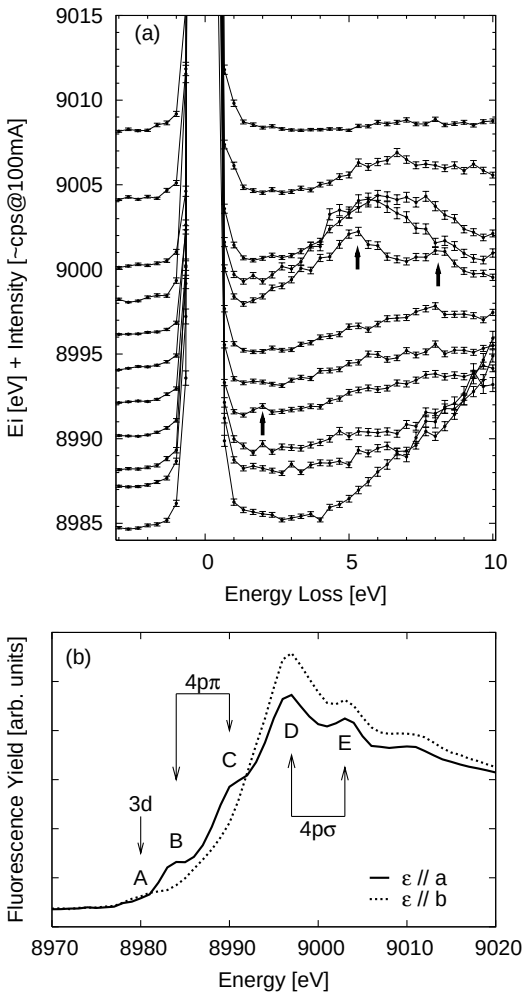

FIG. 1: (a) Resonant inelastic x-ray scattering spectra of $YBa_2Cu_3O_{7-\delta}$ as a function of energy loss at some representative incident x-ray energies (E_i). The scattering vector is fixed at $\boldsymbol{Q} = (4.5, 0, 0)$. Three resonantly enhanced excitations are indicated by the arrows. The strong intensity above 10 eV in the spectrum of $E_i = 8984.5$ eV comes from the Cu $K\beta_5$ emission line. (b) Absorption spectra of twin-free $YBa_2Cu_3O_{7-\delta}$ near the Cu-K absorption edge.

$\boldsymbol{Q} = \boldsymbol{G} + \boldsymbol{q}/2\pi$ of $\boldsymbol{G} = (0, 4, 0)$. Apart from the peak at 5.5 eV, we found two characteristics in the low energy region which are considered the excitations across the Mott gap. One is a broad excitation at 1.5-4 eV which is almost independent of the momentum transfer. The other is an excitation at 2 eV which is prominent at the zone boundary of $\boldsymbol{b}^*$ direction, that is, the intensity is enhanced near $(0, \pi)$ and (π, π). We confirmed that these characteristics are independent of the selection of the Brillouin zone. The excitation along the $\boldsymbol{a}^*$- and $\boldsymbol{b}^*$-axes should be equivalent in the plane. On the other hand, the momentum dependence along the $\boldsymbol{b}^*$-axis can be larger than that along the $\boldsymbol{a}^*$-axis in the chain, because the chain runs along the $\boldsymbol{b}$-axis. Accordingly, clear

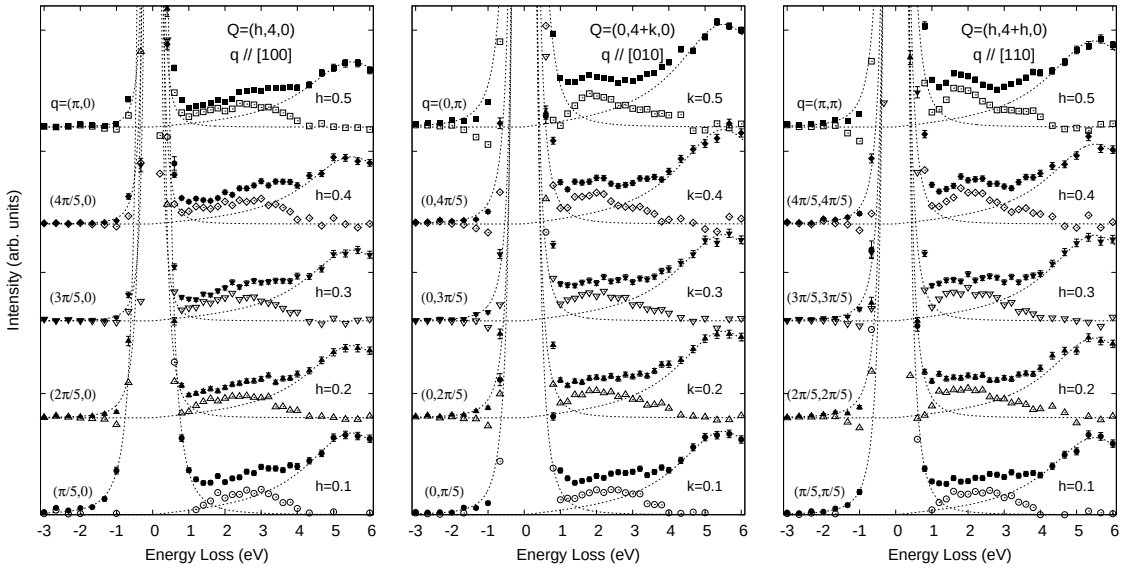

FIG. 2: Momentum dependence of the RIXS spectra. The energy of incident x-ray is 8990 eV. The filled marks are the raw data, and the open marks are the data from which the elastic scattering and the peak at 5.5 eV indicated by dotted lines are subtracted.

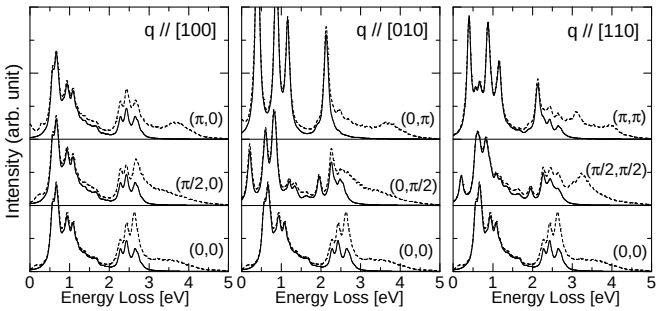

FIG. 3: Theoretical result of the momentum dependence of the chain component of the RIXS presented by solid lines. The left, middle, and right panels show the spectra along [100], [010], and [110], respectively. The dotted lines denote the spectra which are summed up with the chain and the plane components, where the plane component is the same as shown in Ref. [21]. The model parameters for the chain are $U/t = 4$, $U_c/t = 6$. and $\Gamma/t = 1$ with $t = 0.3$ eV. The δ-functions are convoluted with Lorentzian broadening of $0.2t$.

momentum dependence along the $\boldsymbol{b}^*$-axis of 2 eV peak is a direct evidence that this is the excitation across the Mott gap in the chain, while the broad feature at 1.5-4 eV is the excitation in the plane.

In order to consider the origin of the peak structures more accurately, we carried out the calculation of the RIXS spectrum by using the numerically exact diagonalization technique on small clusters [21]. We consider the one-dimensional Hubbard model for the CuO_3 chain, where the Zhang-Rice band (ZRB) is regarded as the lower Hubbard band (LHB). The model includes the hopping term of the electrons (t) and the on-site Coulomb interaction term (U). Because the band calculations and the angle-resolved photoemission indicate that the filling of the electrons on the chain is close to one quarter [10, 22], we adopt the filling in the twelve-site Hubbard chain. The RIXS spectrum is expressed as the second-order process of the dipole-transition between Cu 1s and 4p orbitals, where the Coulomb interaction (U_c) between Cu 1s core-hole and the '3d-system' is explicitly included in the process. The values of the model parameters are set to be $U/t = 4$, $U_c/t = 6$, and $\Gamma/t = 1$ with $t = 0.3$ eV where Γ is the inverse of the life time of the intermediate state, in order for the theoretical data to reproduce the 2 eV structure in Fig. 2. In order to choose the incident energy for the RIXS calculation, we first calculated the x-ray absorption spectrum (not shown here) expressed by the Eq. 3 in Ref. [23], and found the three-peak structure as similar to that of the hole-doped two-dimensional case [23]: The peaks of the well-screened and the poorly-screened states are located at around $\omega = U - 2U_c$ and $-U_c$, respectively, and the peak that the core-hole is created at the hole-doped sites is located at around 0. The incident energy of 8990 eV in the experiment is suggested to be set to the energy of the poorly-screened state, and thus the incident energy for the calculation is chosen to the energy of the poorly-screened state.

Figure 3 shows the theoretical result of the RIXS for the chain (solid lines), together with the spectrum which is summed up with the chain and the plane components (dotted lines). Here the spectrum for the plane is the same as shown in Ref. [24]. The spectrum with zero momentum transfer of the chain site is plotted for all the momenta along [100] (the left panel in Fig. 3). The spec-

trum along [110] is the average of spectra along [100] and [010]. The spectrum below the energy $\Delta\omega \sim 4t = 1.2$ eV ($4t$ is the band width of the free electron) is due to the excitation within LHB, which is swallowed up by the quasielastic peak. Note that its spectral weight is extremely reduced when the incident energy is set to that of the well-screened state and this feature may be observed by handling with much better energy resolution in future. The spectrum above $\sim 4t$ is due to the excitation from the LHB to the upper Hubbard band (UHB). At $(0, 0)$, it spreads over the energy region between 2 and 3 eV. The spectrum becomes more intensive with increasing the momentum transfer of the chain state, and the spectral weight concentrates in the narrow energy region at $(0, \pi)$. The feature is similar to that in undoped chain case [24]. We consider that this intensive feature for the chain component appears as the peak structure of 2 eV in the experimental data.

As shown by the dotted lines in Fig. 3, there appear broad spectra in the energy region up to the 4 eV, which originate from the Mott gap excitation in the plane [23]. The broad-peak structures correspond to the broad excitations at 1.5-4 eV seen in Fig. 2. The broad feature of the Mott gap excitations in hole-doped CuO_2 plane in $YBa_2Cu_3O_{7-\delta}$ is quite contrast to that of the undoped one in $Ca_2CuO_2Cl_2$ [11] and La_2CuO_4 [13], in which a sharp peak can be seen at 2-4 eV. We can estimate the magnitude of the dispersion in the plane from the spectra along the [100] direction in Fig. 2 because of no dispersion in the chain along this direction, and it is much smaller than that in undoped ones. The smaller dispersion in hole-doped CuO_2 plane has been predicted in the theoretical calculation [23].

Our experimental results and theoretical calculations demonstrate that the charge gap of the chain is smaller than that of the plane. In order to compare the theoretical peak position at $(0, \pi)$ with that of the experimental data, we have to set the value of U to $4t$ for the chain rather than the value of $10t$ for the plane. The small value of U suggests that the charge transfer parameter Δ of the chain is small compared with that of the plane. The reason of the different values of Δ's is because the Cu atom in the plane has five ligand oxygen while the Cu in the chain has four, so that the electric environment around the Cu and O sites of the chain is different from that of the plane [25]. Optical measurements for insulating cuprates show that the charge transfer gap decreases with decreasing the number of ligand oxygen [26], which is consistent with the present case. We also note that the small Δ for the chain is consistent with a recent study [9], where it is shown that the $2k_F$ Friedel oscillation of the charge density, instead of $4k_F$ one, dominates with small Δ and it is discussed that the oscillation can offer the explanation of STM results [5, 6, 7].

Individual calculations of the chain and the plane reproduce well the experimental spectra. This may suggest that the coupling between the CuO chain and the neighboring CuO_2 planes is rather weak.

In summary, we have performed a RIXS study for the optimally doped $YBa_2Cu_3O_{7-\delta}$, and found two characteristic excitations. The excitation from the CuO_2 chain shows broad feature at 1.5-4 eV and is almost independent of the momentum transfer, which is consistent with the theoretical prediction. On the other hand, the excitation from the CuO chain is enhanced at 2 eV near the zone boundary of the $\boldsymbol{b}^*$ direction. The result indicates that the Mott gap in the chain is smaller than that in the plane, and provides an important constraint to understand how the CuO chain plays a role in the superconductivity of YBCO.

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[1] B. Koch, H. P. Geserich, and T. Wolf, Solid State Comm. **71**, 495 (1989).
[2] K. Takenaka, K. Mizuhashi, H. Takagi, and S. Uchida, Phys. Rev. B **50**, 6534 (1994).
[3] D. N. Basov *et al.*, Phys. Rev. Lett. **74**, 598 (1995).
[4] R. Gagnon, S. Pu, B. Ellman, and L. Taillefer, Phys. Rev. Lett. **78**, 1976 (1997).
[5] H. L. Edwards, A. L. Barr, J. T. Markert, and A. L. de Lozanne, Phy. Rev. Lett. **73**, 1154 (1994).
[6] D. J. Derro *et al.*, Phy. Rev. Lett. **88**, 097002 (2002).
[7] M. Maki, T. Nishizaki, K. Shibata, and N. Kobayashi, Phy. Rev. B **65**, 140511 (2002).
[8] D. K. Morr and A. V. Balatsky, Phys. Rev. Lett. **90**, 067005 (2003).
[9] M. Mori, T. Tohyama, S. Maekawa, and J. A. Riera, Phy. Rev. B **69**, 014513 (2004).
[10] D. H. Lu *et al.*, Phy. Rev. Lett. **86**, 4370 (2001).
[11] M. Z. Hasan *et al.*, Science **288**, 1811 (2000).
[12] M. Z. Hasan *et al.*, Phys. Rev. Lett. **88**, 177403 (2002).
[13] Y. J. Kim *et al.*, Phys. Rev. Lett. **89**, 177003 (2002).
[14] Y.-J. Kim *et al.*, Phys. Rev. Lett. **92**, 137402 (2004).
[15] Y.-J. Kim *et al.*, Phys. Rev. B **69**, 155105 (2004).
[16] T. Inami *et al.*, Phys. Rev. B **67**, 045108 (2003).
[17] K. Ishii *et al.*, cond-mat/0405209.
[18] T. Inami *et al.*, Nucl. Inst. & Mech. in Phys. Res. A **467-468**, 1081 (2001).
[19] Y. Yamada and Y. Shohara, Physica C **217**, 182 (1993).
[20] N. Kosugi, Y. Tokura, H. Takagi, and S. Uchida, Phys. Rev. B **41**, 131 (1990).
[21] K. Tsutsui, T. Tohyama, and S. Maekawa, Phys. Rev. Lett. **83**, 3705 (1999).

[22] W. E. Pickett, R. E. Cohen, and H. Krakauer, Phy. Rev. B **42**, 8764 (1990).
[23] K. Tsutsui, T. Tohyama, and S. Maekawa, Phys. Rev. Lett. **91**, 117001 (2003).
[24] K. Tsutsui, T. Tohyama, and S. Maekawa, Phys. Rev. B **61**, 7180 (2000).
[25] Y. Ohta, T. Tohyama, and S. Maekawa, Phys. Rev. Lett. **66**, 1228 (1991).
[26] Y. Tokura *et al.*, Phys. Rev. B **41**, 11657 (1990).